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# Relaxation and crystal nucleation in polymer glasses

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ABSTRACT

Depending on the degree of undercooling, polymers crystallize from heterogeneous or homogeneous nuclei. The volume density of homogeneous nuclei at deep undercooling is often several orders of magnitude larger than that of heterogeneous nuclei; allowing crystallization even below the glass transition temperature. With the introduction of fast scanning chip calorimetry (FSC) detailed studies of nucleation and eventually crystallization at such low temperatures (deep undercooling) became possible. Homogeneous nucleation at temperatures below the glass transition shows an unexpected feature in regard to enthalpy relaxation occurring in the same temperature range. As a result of the often fast quench, the glass is initially in a high-enthalpy state causing enthalpy relaxation. Even if the mobility in the material is high, formation of overcritical nuclei is not immediately observed. Only after completion of the enthalpy relaxation, in other words, when the enthalpy of the supercooled liquid state is reached, homogeneous nucleation is observed. On the example of several polymers with different crystallization rates, we show that this behavior seems to be general.

## 1. General information

Fast scanning chip calorimetry (FSC), first reported more than 20 years ago [1–3], and later on adapted for analysis of polymer crystallization, reorganization, and melting [4–7] has frequently been used to gain information about critical cooling conditions required to obtain polymeric glasses free of crystals and free of homogeneous nuclei. These cooling conditions often exceed the instrument capabilities of conventional differential scanning calorimetry (DSC) [8–10], are polymer-specific and listed in recent reviews [11,12]. The observation of well-defined glasses forming on vitrification of the melt at precisely controlled supercritical cooling rates provides then the unique opportunity to study their instability with respect to possible structural changes towards equilibrium. Such structural changes include densification/enthalpy relaxation of the glass [13–15], and formation of crystal nuclei and eventually of crystals [16–18].

The non-equilibrium nature of a glass immediately after vitrification of the melt is often schematically illustrated by plotting the specific volume or the enthalpy of the system as a function of temperature during cooling and subsequent isothermal annealing, as shown in Fig. 1. During cooling the polymer melt, at high temperature its enthalpy decreases independently of the applied cooling rate due to the sufficiently short relaxation time of the system (solid black line). At the glass transition temperature $T_g$, the enthalpy of the system begins to deviate from the extrapolated value of the liquid phase (black dashed line) and remains at higher level (gray curves), caused by the much increased relaxation time. The polymer is then in the glassy state, with $T_g$, however, depending on the rate of cooling. Typically, at common DSC cooling rates of the order of 10 K/min, it is found that an increase of the cooling rate by one order of magnitude leads to an increase of $T_g$ by 3–5 K [19–23]. As such, by variation of the cooling rate, glasses of different enthalpy and therefore degree of instability can be generated, as it is indicated with the various gray curves; with increasing rate of cooling the liquid, the enthalpy of the glass is increasing.

Instability of glasses is proven by relaxation processes which straightforwardly may be analyzed by annealing experiments. In the example of Fig. 1, annealing is performed isothermally at the temperature $T_a$ with the vertical arrow indicating that the enthalpy of the glass (gray circle) decreases towards the value of the liquid phase at identical temperature (black circle). The decrease of the enthalpy, often called enthalpy relaxation, depends on time, with the kinetics experimentally assessable if $T_a$ is only few Kelvin below $T_g$; note that recent analysis of old fossil resins available in nature permitted obtaining new information about aging far below $T_g$ [24]. In one of the simplest approaches [25], the time-evolution of the decrease of the enthalpy $H$ during annealing can be described using Eq. (1):

$$\Delta H_{relax}(T_a, t) = \Delta H_{relax,\,max}(T_a)[1-\exp[-(t/\tau)^{\beta}]] \quad (1a)$$

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